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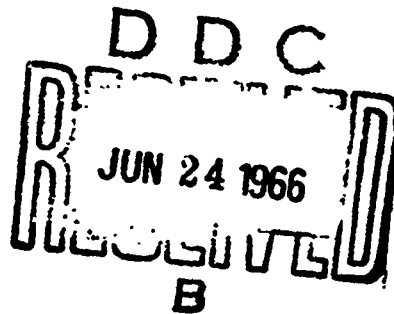
TYCO LABORATORIES, INC.
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MATERIALS RESEARCH LABORATORY
Waltham 54, Massachusetts

April 27, 1962

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Dear Sir:



We are enclosing for your attention one reproducible copy and, under separate cover, 114 additional copies of the Final Technical Summary Report on Electrochemistry of Fuel Cell Electrodes:

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by A. I. Mlavsky
A. I. Mlavsky, Assistant
Technical Director

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Final Technical Summary Report on Electrochemistry of Fuel Cell Electrodes

ABSTRACT

In an attempt to correlate electrode behavior with the electronic properties of electrode materials with incompletely occupied d-orbitals, a number of intermetallic compounds containing nickel together with an electronegative element from groups IV-B, V-B, and VI-B of periodic tables, have been synthesized and evaluated as electrode materials. NiO, NiS, NiAs, NiSb, NiSi and elemental nickel in the massive form have been studied in N₂, O₂ and H₂ atmospheres in both alkaline and acid perchlorate media. Anodic and cathodic polarization measurements were made. Polarization has been pronounced at moderate current densities. Participation of O₂ and H₂ has been poor and the corrosion reactions have been prominent. The cathodic hydrogen evolution reaction on these electrodes is discussed.

The use of palladium as a support material for quick permeation of hydrogen and avoiding the three-phase interface problem is discussed. Results of the effect of various treatment of the palladium surface on the permeation of hydrogen are presented and discussed.

I. GENERAL INTRODUCTION

The principal objective of the research under this contract is the correlation of electrode behavior with the electronic properties of electrode materials with incompletely occupied d-orbitals. The theoretical approach was based, in part, on the following concept.

Generally speaking, heterogeneous catalysis occurs when a surface reduces the free energy of activation for the transfer of electrons between two or more reacting species. Catalysis at fuel cell electrode surfaces is distinguished, however, by the fact that the catalyst acts as source (or sink) of electrons which are replenished from (or removed to) an external circuit. The potential associated with the electrode, particularly under conditions of current flow, serves as a unique experimental parameter in the study of electron transfer in surface reactions. Thus, in addition to its obvious practical merit, the study of the fuel cell electrode reactions is an important means for exploring the mechanism of electron transfer across phase interfaces. It can thereby illuminate the major problem of surface chemistry, i. e., the dependence of surface reactivity upon the bulk electronic properties of solids.

There is abundant experimental evidence that the catalytic activity of the transition elements and their oxides is related to the formation of chemical bonds between the adsorbed species and the d-orbitals of the surface atoms. A consistent interpretation of these results has been obscured, however, by a generally inadequate theoretical description of the character of the d-orbitals in solids. In the case of the ionic solids, the most satisfactory description is obtained through crystal field theory which assumes localized d-electrons. In the case of the transition metals themselves, a simple qualitative description is the band picture proposed by Bloch and elaborated for transition metals by Mott and Jones.

A general model must involve a synthesis of these two extreme positions, i. e., a model in which the interaction of d-orbitals and the

consequent broadening of the d-states into a band is located as a continuous function of the cation-cation separation and the character of the crystal field. While such a theory has not been evolved, the Pauling valence bond model, modified by the purely hypothetical "metallic orbital", has given a fairly consistent treatment of the bond lengths and the magnetic properties of transition metals and their compounds. Although the Pauling theory gives little insight into the electronic properties of these materials, it does give a useful model by which the chemical activity may be correlated with composition and crystal structure. Beck and others have used this model in elucidating the chemisorption of dry hydrogen on surfaces of the transition metal alloys.

The cation-cation separation and charge can be varied continuously in such structures, as $B_8(NiAs)$, $B_{31}(MnP)$, $B_{20}(FeSi)$, through changes in the anionic composition. This kind of study is likely to yield a definitive experimental basis for the critical evaluation of existing theories of d-orbital interaction and, possibly, to the evolution of a more general theory. A study of the properties of fuel cell electrodes made from these materials could yield an equally significant basis for evaluating the relationship of chemical activity to d-band character.

It was concluded that intercomparison of behavior of selected compounds of nickel provided a fruitful approach, and efforts were made to synthesize a number of nickel compounds with varying ratios of the electron number per nickel atom, within similar structure types, where possible.

Cathodic and anodic polarization measurements were made on massive electrodes in acid and alkaline solutions saturated with H_2 , N_2 and O_2 . The H_2 participation in the anodic reaction and the O_2 participation in the cathodic reaction were limited by gas diffusion limiting current on one hand (high c. d. side) and depolarization due to corrosion and possible impurity reactions on the other (low c. d. side). The results obtained, although they gave useful information on the gas

evolution reactions, failed to do so for gas consumption reactions (viz., anodic oxidation of hydrogen and cathodic reduction of oxygen) and therefore illustrate the need for a new approach to the problem. There are three possibilities:

(1) One obvious experimental means is the use of ultrapure systems. Although this would permit the use of massive electrodes, and would lead to a valid determination of the electrochemical parameter α , it is very tedious and should be reserved for materials of demonstrable promise.

(2) An alternative approach is required for screening new electrode compositions; this clearly must involve the use of high specific area electrodes. A detailed scientific analysis of the results obtained will be difficult because of uncertainties in the transport rates and the true surface area. Nevertheless, as long as the conditions of the electrode preparation are carefully reproduced, a correlation of electrode composition and the electrochemical parameters should be qualitatively valid. The high specific area electrodes will thus be extremely useful in screening new materials and would have an immediate practical advantage should promising new materials be found. If and when the latter are found, a return to massive electrodes and ultrapure systems could be undertaken for a precise clarification of the relevant electrochemical mechanisms. Work in this area was initiated at the end of the contract period.

(3) The use of palladium as a support for diffusion hydrogen electrode (anode) has distinct advantages in that palladium allows rapid permeation of hydrogen through, and also one avoids the three-phase interface problem confronted in the conventional porous electrodes. Various catalyst materials can be deposited on the palladium surface and their electrocatalytic properties studied. Although only hydrogen gas can be used in such a system, the scientific information obtained thus should be very valuable. Work in this area was initiated and the results obtained so far are presented in this report.

II. MASSIVE ELECTRODES

A. Introduction:

The electrode materials examined were Ni, NiSi, NiSb, NiAs, NiS, NiO (Li doped 5%), ZnO (Li doped 2%), bright Pt, and platinized platinum.

The electrolytes used were:

Acid: 1 M HClO_4
Alkali: 0.01 M NaOH + 1 M NaClO_4 pH = 10.8
also 6 M KOH where stated
Neutral: Phosphate buffer pH = 7.

The details of the experimental technique have been previously reported.^{1, 2, 3} The results have also been previously reported^{1, 2, 3}, except for NiO and platinized Pt.

B. Discussion of Results:

The general feature of the results may be summarized as follows:

(1) All the electrode systems deviated from reversibility in regard to their behavior as hydrogen and oxygen electrodes. Deviation was generally larger for oxygen than for hydrogen. In cases where the potential was indifferent to the ambient gases, dissolution reaction was observed.

(2) At low c. d. range, "depolarization" was observed, the reason for which is ascribable to corrosion (dissolution)-type reactions and impurity reactions. The effect of impurities was obviated from low c. d. results obtained for Ni and Pt in alkaline solutions where corrosion reaction is known not to interfere with reversible hydrogen electrode behavior.

(3) On the anodic side, corrosion and dissolution-type reactions at low c. d. range were followed by oxygen evolution-type reactions on passivated surfaces. NiS, NiAs and ZnO electrodes showed strong signs of attack and no passivation was observed. Large hysteresis effects were observed between runs of increasing and de-

creasing c. d. 's. No simple Tafel behavior was obtained on the anodic oxygen evolution reactions except on Ni and Pt.

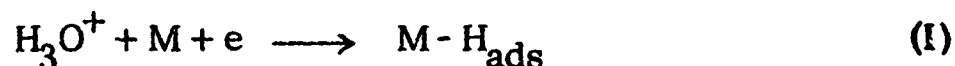
(4) Oxygen participation on the cathodic side, and hydrogen participation on the anodic side were not pronounced.

(5) NiO (Li doped 5%) electrode which was examined more recently both in acid and alkaline solutions showed poor polarization behavior as a fuel cell electrode. The electrode was easily polarized and the rise of potential was very slow. The results appear to show rise in the resistivity of the electrode sample during current flow.

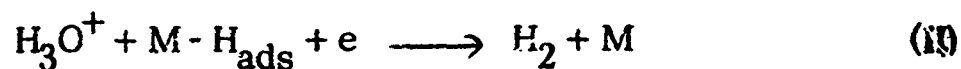
(6) Although showing signs of depolarization at low c. d. range, most of the electrodes gave good Tafel behavior for hydrogen evolution reaction at the moderately high cathodic c. d. range. These results presented in earlier reports^{1, 2} merit some comment.

The exchange current i_0 (obtained from extrapolation of the Tafel line to zero overpotential) is taken as a measure of the electrochemical activity of the electrode and the Tafel slope b as a parameter symptomatic of the reaction mechanism. In Table 1 these parameters are presented with certain other properties of the electrode materials.

The b values are of the same order and indicate either a rate-controlling discharge mechanism,



or a rate-controlling ion-atom combination reaction,



both mechanisms taking the same b value under certain conditions. From our present results, it is not possible to distinguish between the two mechanisms. It has, however, been shown by careful work⁴ that on nickel the mechanism II is rate-controlling.

In alkaline solutions, the i_0 values are of the same order, except for NiAs. A similar order is observed in acid solutions. A simple explanation does not seem possible for the very low exchange

current for NiAs. It has been shown, however, that the presence of arsenic in the form of its soluble salts in the electrolyte acts as a poison for hydrogen evolution reaction on Ag and Ni, and that when present in large amounts, retards the reaction.

The electrocatalytic activity (its measure being expressed as exchange current here) may depend on two factors: firstly, the "atom" itself, irrespective of the electronic environment; and secondly, the electronic environment itself. In the present case, the "atom" component, viz., nickel, remains common. It is assumed that the cathodic hydrogen evolution reaction takes place predominantly on the "nickel surface". The electronic environment of the electrode materials has been varied to a large extent. This variation was not, however, reflected in a correspondingly large variation in the exchange current values. On the basis of the above argument, the results presented in Table 1 would show that the atom is more important than the electronic environment. Two other important properties, viz., heat of adsorption of hydrogen and the electronic work function (Fermi level) for these materials must also be considered. Since these values are not available and our experimental results are not very precise, the above conclusions should be considered tentative.

TABLE 1
HYDROGEN EVOLUTION REACTION

Electrode Material	$-\log i_0 (\text{A/cm}^2)$	$b(v)$	Valence of the negative element	Electroneg- ativity of the negative element ²²	Heat of Formation ²³ H_f (kcal/mol)	r^*
<u>Alkali:</u>						
Ni	5.6	0.094	-	-	-	1
NiSi	5.1	0.117	4	1.8	-	-
NiAs	10	0.110	5	2.0	6.5(?)	1.39
NiS	5	0.130	5	2.5	11.1	1.55
<u>Acid:</u>						
Ni	5.4	0.127	-	-	-	1
NiSi	6.9	0.105	4	1.8	-	-
NiSb	7.4	0.115	5	1.8	7.9	1.31

* r = axial ratio²³

III. PALLADIUM-HYDROGEN SYSTEM

A. Brief Literature Review:

(1) Introduction:

The general phenomena of diffusion of gases through metals have been the subject of much work since Graham discovered in 1866 that hydrogen could diffuse through platinum. An extensive body of experimental information exists regarding the permeation of hydrogen through palladium from gas phase to vacuum. Work has also been done on the adsorption of hydrogen dissolved in electrolytes by palladium immersed in the electrolytes. More recently, attention has been given to the electrochemical properties of metal surfaces through which hydrogen is allowed to diffuse.

(2) Permeation of Hydrogen from Gas Phase to Vacuum:

(a) Experimental Facts: In 1904 Richardson, Nicol and Parnell⁵ arrived at the equation for the permeation of a gas through a metal,

$$P = k/d p^{1/2} T^{1/2} e^{-b/T}$$

(known as the Richardson equation), when the gas is maintained at a pressure, p , on one side of the metal while a vacuum is on the other, and where k and b are constants, T absolute temperature, and d is the thickness of the metal. Their data for the Pt/H system were in agreement with their equation. In 1935 Smithells and Ransley⁶ examined their own data as well as all previously published data on various metal/gas systems for wide ranges of temperatures and pressures, and found in general a good agreement with Richardson's equation. The plots of $\log P$ vs. $1/T$ gave excellent straight lines, so also in plots of P vs. $p^{1/2}$ at higher pressures. At lower pressures, the rate of permeation was found to be less than that required by the equation. The concept that diffusion is preceded by adsorption was examined and by incorporating a factor for the

fraction of the surface covered (Langmuir isotherm), they derived the equation at constant temperature,

$$P = k'p^{1/2} \left(\frac{ap}{1+ap} \right)$$

At high pressures, the term in brackets approaches unity and the equation approximates the original equation. At low pressures the rate of permeation falls off as has been observed experimentally. They compared values for the constant "a" as derived from this equation with values obtained from previous direct adsorption studies to uphold this relationship. They also observed increased permeation rate with various surface treatment designed to extend the surface area (viz., oxidation, reduction, etching, etc.) in accordance with rate-controlling adsorption mechanism. They quoted results to show the inverse proportionality with thickness of the metal. Hurlbert and Konecny⁷ examined the relation of thickness to permeation and found that Richardson's equation holds, except for extremely thin membranes (20 microns) where the permeation is determined by the rate of the surface reaction alone. When the thickness was sufficiently large (much higher than 20 microns), the diffusion through the solid was rate-determining.

Darling⁸ found that high permeabilities could be maintained by adding oxygen to the hydrogen and passing an excess of the gas over the metal surface continuously. He concluded that an inert layer of impurity gas rather than surface poisoning was responsible for loss in permeability under static applied pressures. Although an inert gas layer may have affected Darling's results, the possibility of surface poisoning cannot be ruled out.

Davis⁹ found that reproducible permeabilities proportional to \sqrt{p} could be obtained by avoiding any possible contamination. Poisoning the high-pressure face led to a low

average concentration in the metal (as determined by electrical resistivity); poisoning the low-pressure face gave a high average concentration, approaching the value in equilibrium with the fore-pressure. Poisoning the off-side had the greater effect on the permeability. The high permeabilities could be recovered by oxidation in air or oxygen, followed by reduction in hydrogen or by cathodic sputtering. M. Van Swaay and C. E. Birchenall¹⁰ observed similar effects of poisoning.

(b) Theoretical Treatment: In the deduction of Richardson's equation, the process of permeation was considered essentially as a single-step process. Wang¹¹ broke down the process into various steps and also replaced Ransley's erroneous equation for θ by the correct form

$$\theta = \frac{ap^{1/2}}{1 + ap^{1/2}}$$

In addition to these three steps, viz., dissociative adsorption of hydrogen on the pressure face, diffusion through the bulk metal phase and the associative desorption on the off-face, he considered the possible step of a hydrogen molecule striking the pressure-face and splitting up into one atom adsorbed on the surface and one going inside the metal phase. His deduction correctly predicted the experimental behavior of the \sqrt{p} relationship of the permeability at higher pressures and direct proportionality to p at lower pressures. At infinitely high pressure his expression would indicate infinite permeability contrary to experimental findings. Barrer¹² later modified Wang's rate equations by making allowances for saturation concentrations. This modification indicated that the permeation rate would remain always finite, however large the pressure may be.

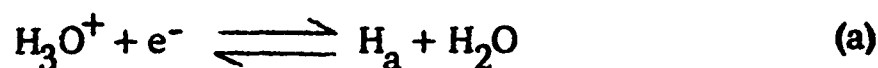
T. G. Owe Berg¹³ has calculated the detailed kinetics of the catalysis by water of the dissociation of hydrogen molecules prior to adsorption. Experimental support is claimed to have been obtained for the description of hydrogen from steel (Hudson et al¹⁴).

(3) Occlusion of Hydrogen by Palladium in Contact with Solutions:

Schuldiner, Castellan and Hoare¹⁵, working under very pure conditions, observed a potential difference of 0.050 V between a palladium electrode and Pt/H₂ electrode in the same hydrogen-stirred acid solution (palladium more noble). They claim that the potential difference eventually will go to zero if impurities are not eliminated carefully. They also report that a pure palladium electrode after an initial anodic treatment reaches the 0.050 V potential as the H/Pd atom ratio rises from zero to 0.03; after reaching those values, both the potential and the atom ratio do not vary with time. To explain this sudden halt of the occlusion of hydrogen, they postulate that when the H/Pd ratio reaches the value of 0.03, the potential of zero charge of the alloy changes in such a way as to change the sign of the double layer on the palladium surface. This change in the sign of the double layer potential difference produces a reorientation of the water dipoles at the surface and this is considered to block further occlusion of hydrogen. Flanagan and Lewis¹⁶ observed that the occlusion of hydrogen does not stop at the H/Pd ratio of 0.03, but would continue up to the saturation ratio of 0.68, irrespective of the manner in which previous hydrogen occlusion was effected (electrolysis or hydrogen bubbling). Fallon and Castellan¹⁷ observed a similar behavior in acid and neutral electrolytes. Their experimental data appear to be consistent with the rate-determining diffusion of dissolved hydrogen from the bulk of the solution to the electrode surface.

(4) Anodic Oxidation of Hydrogen Diffusing through Palladium:

Schuldiner¹⁸ made a detailed and systematic study of the electrochemical behavior of the palladium membrane which was a cathode on one side and an anode on the other side. Hydrogen was deposited on the cathodic side, hydrogen diffused through the palladium foil and was oxidized to hydrogen ions on the anodic side. The H/Pd ratio in the Pd electrode was maintained at the α -Pd-H alloy level. The following steps are considered to take place on the cathodic side:



where H_a denotes hydrogen atoms chemisorbed on sites on the cathodic side; H_i , hydrogen atoms adsorbed in the interior of the electrode; and H_i^+ , protons in the interior of the electrode. This reaction mechanism gives a cathodic Tafel slope of 0.059 V at 25°C, which was in good agreement with the experimentally observed value. Analogously, for the same mechanism the anodic Tafel slope should assume the same value. The Tafel section between the reversible region (current proportional to overpotential) and the limiting current was too narrow to allow any valid evaluation of the slope. Schuldiner and Hoare¹⁹ made similar measurements on the transport of hydrogen through palladium-clad electrodes. Since the thickness of the second metal was rather large, what they essentially observed was limiting diffusion of hydrogen through the second metal.

(5) Object of our Present Measurements:

Our eventual object is to study the electrocatalytic activity of various materials on palladium. It was considered proper therefore to study the effect on the diffusion limiting current of various factors: pH of the solution, previous history of the electrode, etc.

B. Experimental:

(1) Apparatus:

The cell shown in Figure 1 was a pyrex beaker; the electrode a palladium thimble (.25 mm thick, surface area 3.9 cm^2) with hydrogen supplied to the inside of the thimble and provided with a bleeder system; the counter electrode a platinized platinum spiral housed in a tube with a fritted disc bottom; the reference electrode a Pt/H₂ electrode in the same solution. N₂ was bubbled through the cell.

(2) Methods:

Current potential measurements were made, both cathodic and anodic, utilizing constant current and constant potential (potentiostatic) techniques. 0.1, 1, 2, and 5 N H₂SO₄ were used with and without addition of excess neutral salt (Na₂SO₄).

C. Results and Discussion:

The general nature of the results can be summarized as follows:

(1) A fresh palladium electrode immersed in the solution would attain a constant potential of 0.050 V (more noble w. r. t. Pt/H₂). This value will persist after cathodic polarization. The same is true for anodic polarization unless the potential is kept in the oxygen evolution region for long (see later).

(2) The general current/potential behavior observed, both cathodic and anodic, is similar to what was reported by Schuldiner²⁰ for palladium electrodes. The exchange current was of the same order in all the solutions. (Fig. 2)

(3) On the anodic side, when limiting current was reached, the potential changes rapidly to more anodic values. Two steps were recognizable: oxidation of the palladium surface (change of color visually observable) followed by oxygen evolution after which the change of potential with time was very slow. The decay curve on current interruption clearly shows the oxide decomposition step

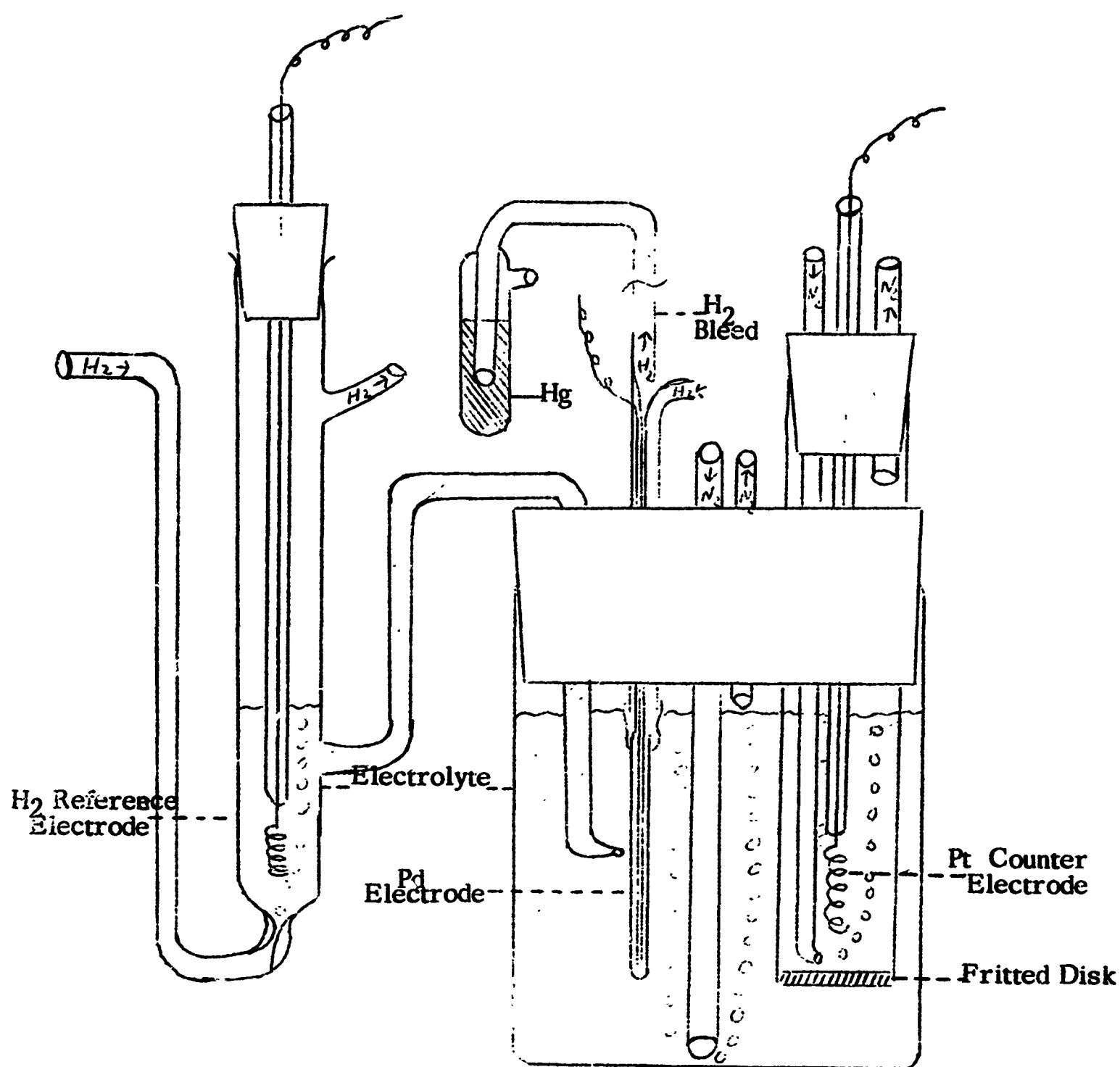


Fig. 1 CELL for Pd/H SYSTEM

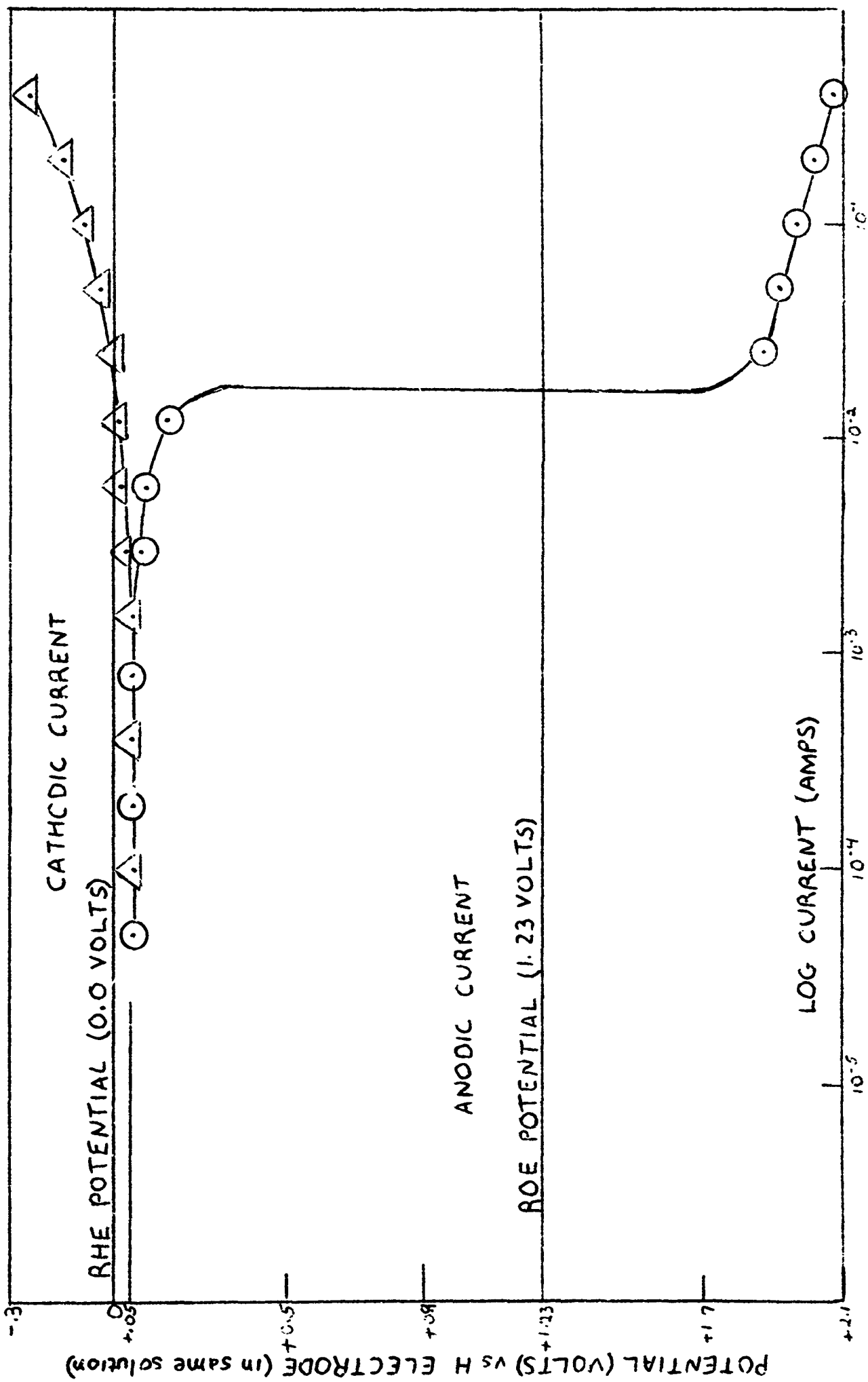


Fig. 2 POLARIZATION CURVE: Pd in 2N H₂SO₄, H₂ ATM.

(compare Hickling and Vrjosek²¹).

(4) With other conditions remaining the same, the anodic limiting current (l. c.) is dependent on the previous history of the electrode. With a fresh electrode (no previous anodic or cathodic treatment) having shown a resting potential of 0.050 V vs. reversible hydrogen electrode (RHE) in the same solution, the l. c. was very reproducible showing no hysteresis effect during "up" and "down" runs, provided that the electrode was not kept above the reversible oxygen electrode (ROE) potential for too long. For example, for an electrode showing a l. c. of 25 ma, the time limit was observed to be about six minutes for a current of 400 ma. The smaller the current, the longer the time limit. In such a case, the resting potential after interruption of the anodic current returned fairly quickly to the usual value of 0.050 V. Once, however, the l. c. is attained and the electrode is allowed to stay above the ROE potential (oxygen evolution preceded by oxide formation) for longer than about six minutes at 400 ma, there is a large hysteresis effect, i. e., considerable lowering of the l. c., (approximately 1.5 ma) during the descending ("down") run. In such a case the resting potential on current interruption is always more positive (noble) than 0.050 V. The electrode, in this state, would show a lower l. c. during a second cycle of runs. The electrode can, however, be restored to its original state by passing cathodic current (hydrogen evolution). An electrode freshly cathodically treated would thus show an anodic l. c. during an "up" run much larger than for a fresh electrode; the larger the cathodic electricity passed, the greater the increase in the anodic l. c. The electrode would then go back to the original l. c. value for a fresh electrode, provided that the electrode is treated anodically above the ROE potential for not too long.

It appears reasonable to suppose that the lowering of the l. c. is due to the formation of a barrier to the path of hydrogen diffusion, and the formation of such a barrier on the anodic treatment may be

due to one of the two effects, viz. , deposition of impurities on the electrode surface and secondly, formation of an oxide on the surface. Let it be assumed that the impurities, if formed, can be removed by cathodic treatment either by mechanical agitation due to hydrogen evolution or by electrochemical reduction to harmless products. A similar assumption appears equally valid for the anodic treatment as well. But vigorous oxygen evolution and the possibility of electrochemical oxidation does not appear to restore the electrode to its normal behavior, rather, the l. c. is irrevocably reduced. The oxide hypothesis appears to be a better explanation for the phenomenon. But the decay curves (plot of potential vs. time on interruption of anodic current above l. c.) showed a definite break at the oxide potential range, indicating the decomposition of the surface oxide. In order to retain the validity of the oxide hypothesis, one must here also assume that the oxide, thus formed and on which oxygen gas was evolved, does not decompose at the thermodynamic potential and that it becomes an electronic conductor (semiconductor). The resting potential for such an electrode (more positive than 0.05⁰ V) is a "mixed" potential, the contributions being made by the oxide potential on one side and the usual Pd/H electrode potential on the other. To prove finally that this is not an impurity effect, experiments should be done in highly purified systems (preelectrolysis of the solution, etc.). Plans are under way to do this in the continuation of the program under a different contract.

IV. IMPREGNATED POROUS CARBON ELECTRODES:

As mentioned earlier, work in this area was initiated at the end of the contract period. A new plexiglass cell was designed and constructed (see Fig. 3). Two grades of carbon discs (F.C. 14 and F.C. 26) supplied by Pure Carbon Company, are being used. The discs of a particular grade are from a single batch. The discs were cleaned ultrasonically, dried in vacuum (20 micron) at an elevated temperature. The catalyst solution of a given concentration (10%) was kept frozen in another part of the setup while the drying (degassing) process was going on and finally thawed and tipped over to the discs when cooled to room temperature. This process was followed by subjecting the discs while immersed in the same solution to a pressure of 100 atm N_2 for one hour. The impregnated discs were dried at $85^\circ C$ under vacuum and were subsequently reduced in hydrogen atmosphere at $450^\circ C$ for one hour. The discs were stored in a vacuum dessicator until use.

The polarization results so far obtained in 5M KOH, though promising, are not yet in a shape for final presentation.

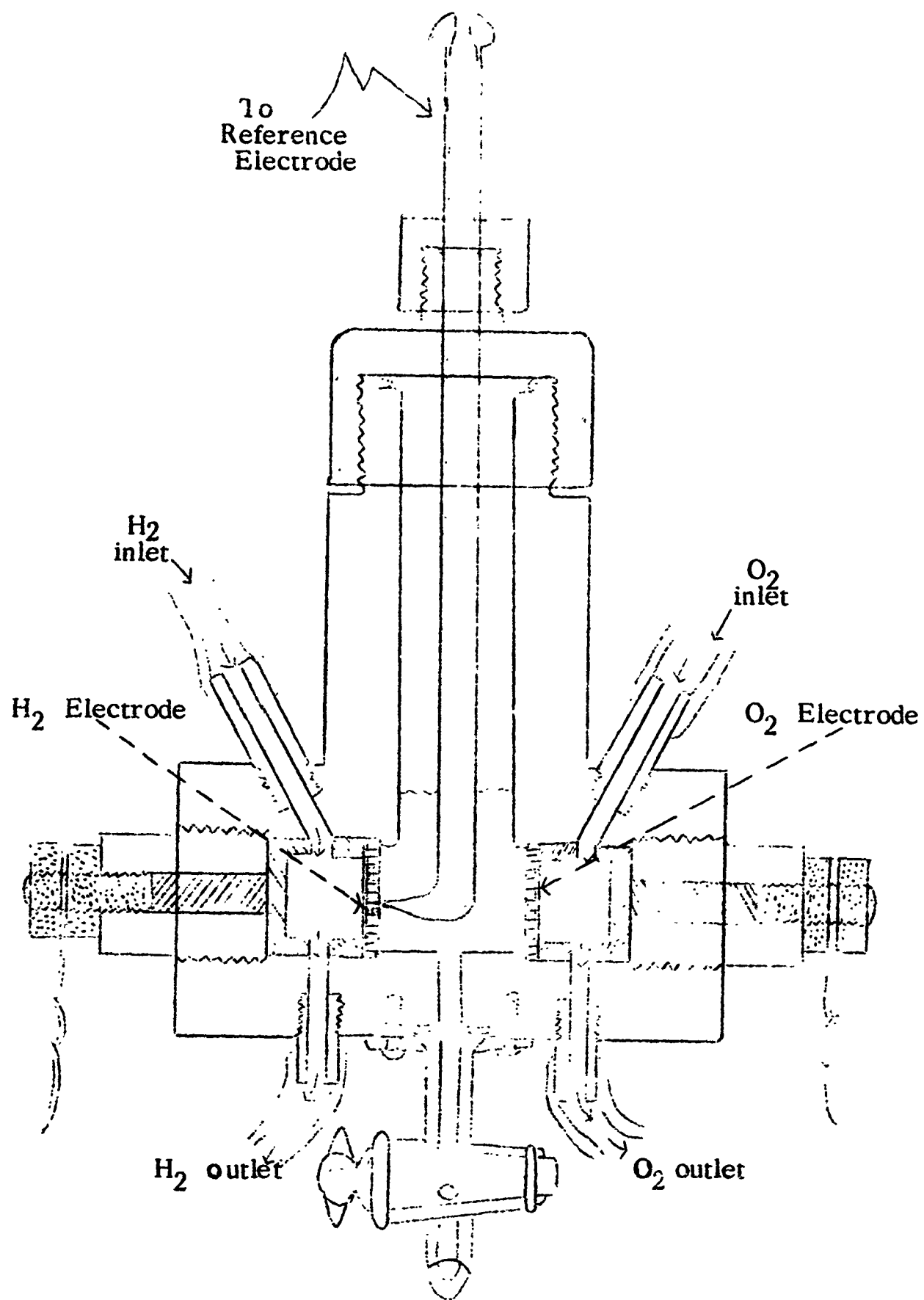


Fig. 3 FUEL CELL for POROUS ELECTRODE

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